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(54) Titre : SYNTHÈSE DE LUBRIFIANTS A BASE DE DIESTERS A PARTIR D'EPOXYDES OBTENUS PAR VOIE ENZYMATIQUE

(54) Title: SYNTHESIS OF DIESTER-BASED LUBRICANTS FROM ENZYMATICALLY-DIRECTED EPOXIDES

**Step 101 - epoxidizing an olefin to form an epoxide
via an enzyme-mediated pathway.**



**Step 102 - directly esterifying the epoxide with a
carboxylic acid to form a diester species.**

Fig. 1

(57) Abrégé/Abstract:

The present invention is generally directed to methods of making diester-based lubricant compositions, wherein formation of diester species proceeds via esterification of epoxide intermediates, and wherein the epoxide intermediates are generated via an



(57) **Abrégé(suite)/Abstract(continued):**

enzymatically-driven mechanism. In some embodiments, the methods for making such diester-based lubricants utilize a biomass precursor and/or low value (e.g., Fischer-Tropsch (FT) olefins and/or alcohols) so as to produce high value diester-based lubricants. In some embodiments, such diester-based lubricants are derived from FT olefins and fatty acids. The fatty acids can be from a bio-based source (i.e., biomass, renewable source) or can be derived from FT alcohols via oxidation.

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(54) Title: SYNTHESIS OF DIESTER-BASED LUBRICANTS FROM ENZYMATICALLY-DIRECTED EPOXIDES

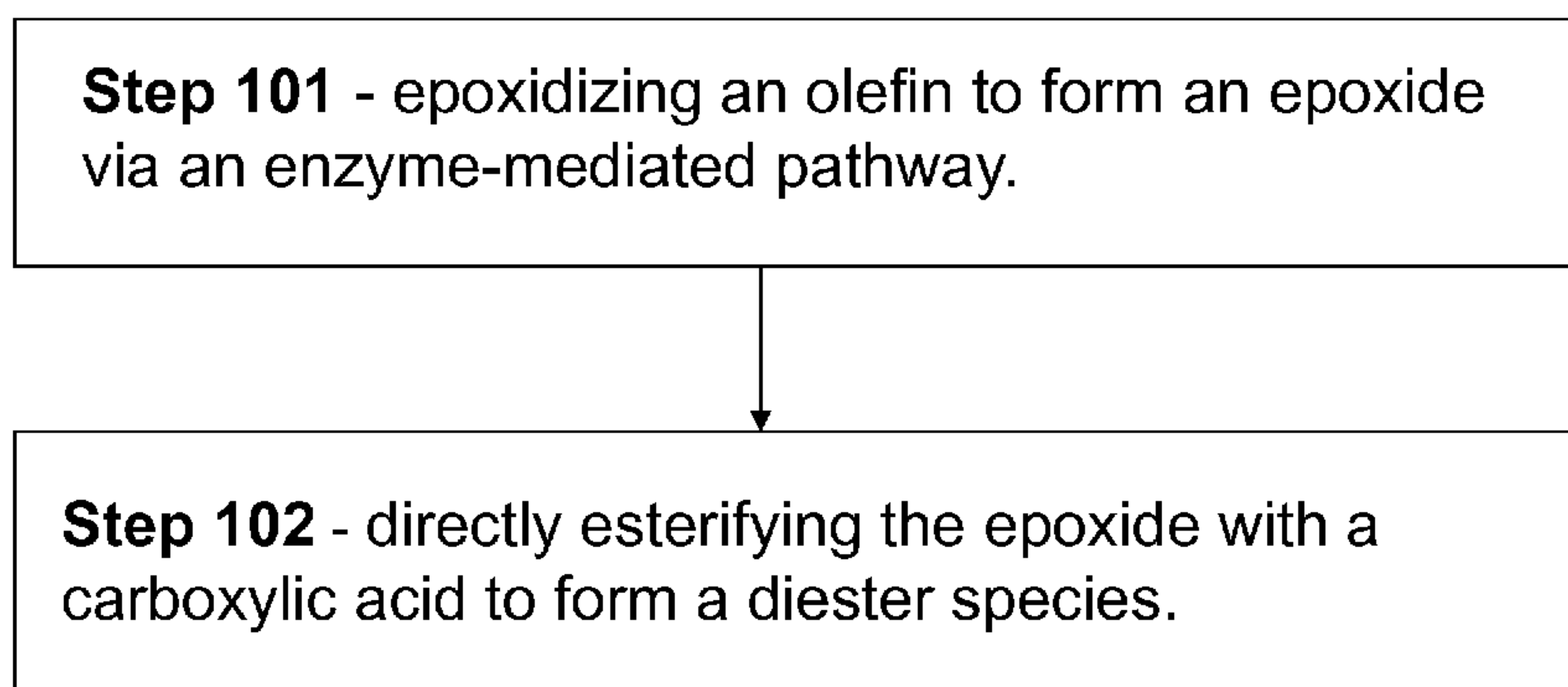


Fig. 1

(57) Abstract: The present invention is generally directed to methods of making diester-based lubricant compositions, wherein formation of diester species proceeds via esterification of epoxide intermediates, and wherein the epoxide intermediates are generated via an enzymatically-driven mechanism. In some embodiments, the methods for making such diester-based lubricants utilize a biomass precursor and/or low value (e.g., Fischer-Tropsch (FT) olefins and/or alcohols) so as to produce high value diester-based lubricants. In some embodiments, such diester-based lubricants are derived from FT olefins and fatty acids. The fatty acids can be from a bio-based source (i.e., biomass, renewable source) or can be derived from FT alcohols via oxidation.

WO 2010/056832 A3

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WO 2010/056832

PCT/US2009/064170

SYNTHESIS OF DIESTER-BASED LUBRICANTS FROM ENZYMATICALLY-DIRECTED EPOXIDES

FIELD OF THE INVENTION

[0001] This invention relates to methods of making ester-based lubricants, and specifically to methods of synthesizing diester-based lubricants via a synthetic route involving enzymatically-directed epoxides.

BACKGROUND

[0002] Esters have been used as lubricating oils for over 50 years. They are used in a variety of applications ranging from jet engines to refrigeration. In fact, esters were the first synthetic crankcase motor oils in automotive applications. However, esters gave way to polyalphaolefins (PAOs) due to the lower cost of PAOs and their formulation similarities to mineral oils. In fully synthetic motor oils, however, esters are almost always used in combination with PAOs to balance the effect on seals, additive solubility, volatility reduction, and energy efficiency improvement by enhanced lubricity.

[0003] Ester-based lubricants, in general, have excellent lubrication properties due to the polarity of the ester molecules of which they are comprised. The polar ester groups of such molecules adhere to metal surfaces creating protective films which slow down the wear and tear of the metal surfaces. Such lubricants are less volatile than the traditional lubricants and tend to have much higher flash points and much lower vapor pressures. Ester lubricants are excellent solvents and dispersants, and can readily solvate and disperse the degradation by-products of oils. Therefore, they greatly reduce sludge buildup. While ester lubricants are stable to thermal and oxidative processes, the ester functionalities give microbes a handle with which to do their biodegrading more efficiently and more effectively than their mineral oil-based analogues—thereby rendering them more environmentally-friendly. However, the preparation of esters is more involved and more costly than the preparation of their PAO counterparts.

[0004] Recently, novel diester-based lubricant compositions and their corresponding syntheses have been described in commonly-assigned United States Patent Application Serial

WO 2010/056832

PCT/US2009/064170

No. 11/673,879; filed February 12, 2007. The synthetic routes described in this patent application comprise and/or generally proceed through the following sequence of reaction steps: (1) epoxidation of an olefin to form an epoxide; (2) conversion of the epoxide to form a diol; and (3) esterification of the diol to form a diester.

[0005] More recently, additionally novel syntheses of the above-mentioned diester-based lubricant compositions have been described in commonly-assigned United States Patent Application Serial No. 12/244,349; filed January 31, 2008. Such syntheses are similar to those described above, but do not proceed through a diol intermediate. Rather, they involve a direct esterification of the epoxide.

[0006] In view of the foregoing, and notwithstanding such above-described advances in diester-based lubricant synthesis, any variation on such above-described methods that can reduce the concentration of the epoxidizing agent(s), increase yields, and/or minimize purification requirements, would be highly beneficial.

BRIEF DESCRIPTION OF THE INVENTION

[0007] The present invention is generally directed to methods of making diester-based lubricant compositions (i.e., lubricant compositions comprising diester species), wherein enzymes are utilized to catalyze or otherwise mediate a portion of the synthesis of the diester species contained therein. In some embodiments, the methods for making such diester-based lubricants utilize a biomass precursor. In these or other embodiments, lubricant precursor species can also be sourced or otherwise derived from Fischer-Tropsch (FT) reaction products and/or the pyrolysis of waste plastic.

[0008] In some or other embodiments, the present invention is directed to processes comprising the steps of (a) epoxidizing an olefin having a carbon number of from 8 to 18 to form an epoxide comprising an epoxide ring, wherein such epoxidation is “enzymatically-driven” by one or more enzymes; and (b) directly esterifying the epoxide with a C₂ to C₁₈ carboxylic acid to form a diester species suitable for use as, and/or for inclusion in, lubricant compositions that have viscosity and pour point operable for use as lubricants. Such direct esterification generally proceeds without the production and isolation of a diol intermediate that is subsequently esterified. Additionally, such epoxidizing and direct esterifying are

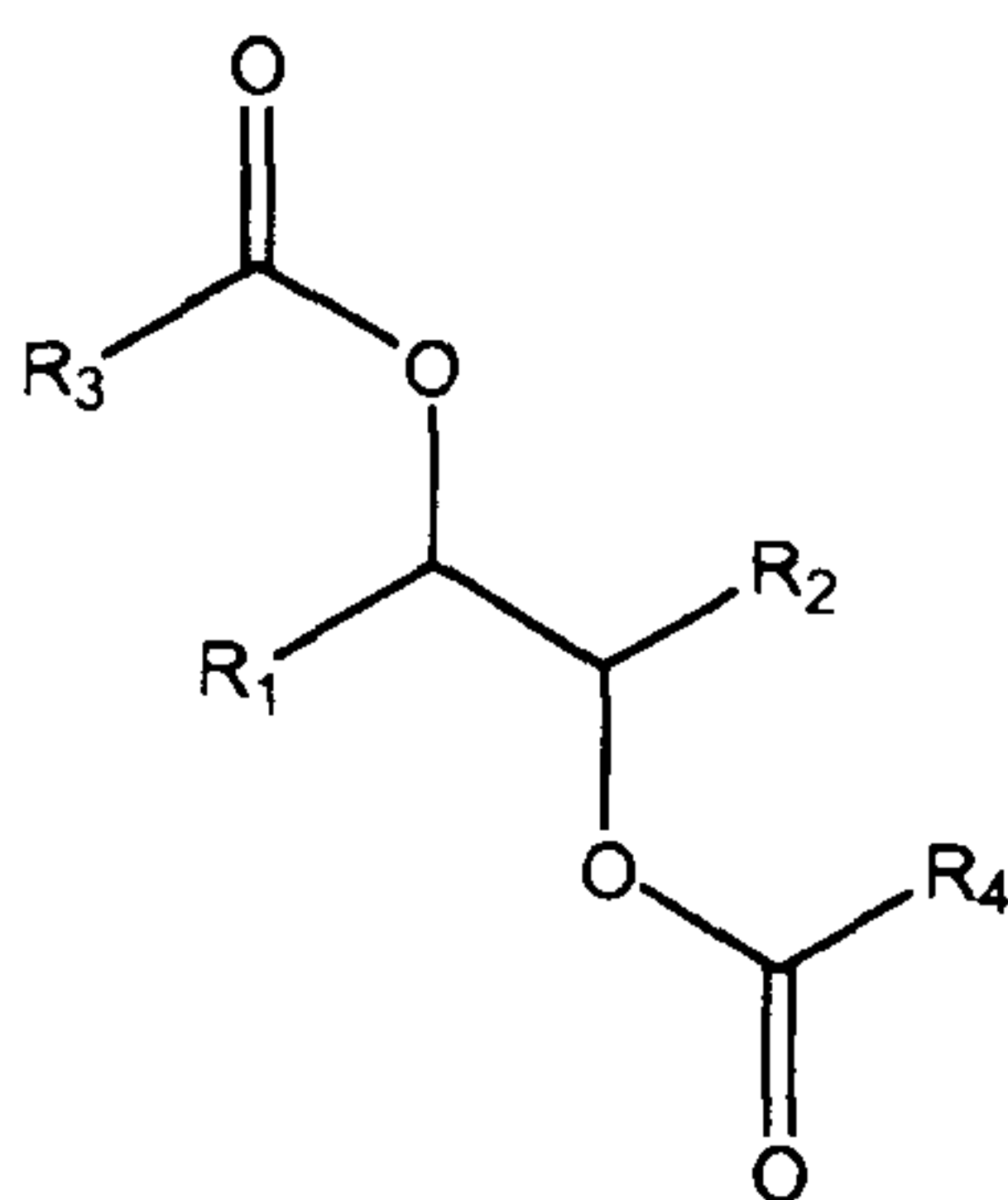
WO 2010/056832

PCT/US2009/064170

typically carried out on a plurality of olefins and epoxides, respectively; and wherein the population of such species can be largely homogeneous or a mixture of such species.

[0009] In some embodiments, the present invention is directed to processes comprising the steps of: (1) epoxidation of an olefin to form an epoxide having a carbon number of from 8 to 16, wherein such epoxidation is enzymatically-driven by one or more enzymes; (2) conversion of the epoxide to form a diol; and (3) esterification of the diol with a C₂ to C₁₈ carboxylic acid to form a diester suitable for use as, and/or for inclusion in, lubricant compositions that have viscosity and pour point operable for use as a lubricant. Additionally, such epoxidizing and direct esterifying are typically carried out on a plurality of olefins and epoxides, respectively; and wherein the population of such species can be largely homogeneous or a mixture of such species.

[0010] Typically, the lubricant compositions produced by the above-mentioned process comprise a quantity of at least one diester species, the diester species having the following structure:



wherein R₁, R₂, R₃, and R₄ are the same or independently selected from C₂ to C₁₇ hydrocarbon groups.

[0011] The foregoing has outlined rather broadly the features of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

WO 2010/056832

PCT/US2009/064170

[0012] For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

[0013] **Fig. 1** is a flow diagram illustrating a method of making diester-based lubricant compositions via an enzymatically-derived epoxide intermediate, wherein the associated synthesis comprises a direct esterification of an epoxide intermediate—in accordance with some embodiments of the present invention;

[0014] **Fig. 2** (Scheme 1) is a chemical flow diagram illustrating an exemplary method of making a diester-based lubricant composition without the production and isolation of a diol intermediate, in accordance with some embodiments of the present invention;

[0015] **Fig. 3** is a flow diagram illustrating a method of making diester-based lubricant compositions via an enzymatically-derived epoxide intermediate that is then converted into a diol en route to a diester species—in accordance with some embodiments of the present invention;

[0016] **Fig. 4** (Scheme 2) is a chemical flow diagram illustrating an exemplary method of making a diester-based lubricant composition via a diol intermediate, in accordance with some embodiments of the present invention;

[0017] **Fig. 5** (Scheme 3) is a chemical flow diagram illustrating enzymatically-directed epoxidation of a mixture of tetradecene isomers, in accordance with some embodiments of the present invention;

[0018] **Fig. 6** (Scheme 4) is a chemical flow diagram illustrating diesterification of a mixture of tetradecene-based epoxides, in accordance with some embodiments of the present invention;

[0019] **Fig. 7** (Table 1) compares the properties of diesters made via tetradecene epoxide intermediates and via tetradecene diol intermediates;

[0020] **Fig. 8** depicts an exemplary mixture of species 1-7 that can be produced via methods of the present invention;

[0021] **Fig. 9** depicts an exemplary species 8, octanoic acid 2-octanoyloxy-dodecyl ester, that can be produced via methods of the present invention; and

WO 2010/056832

PCT/US2009/064170

[0022] Fig. 10 depicts two diester-based compounds 9 and 10, that can be prepared via methods of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

1. Introduction

[0023] As mentioned in a preceding section, the present invention is directed to methods of making diester-based lubricant compositions, wherein such methods include an enzymatically-derived epoxide intermediate, i.e., a step whereby an epoxide intermediate is enzymatically-derived. In some embodiments, such methods for making such diester-based lubricants utilize a biomass precursor and/or low value olefins and/or alcohols (e.g., those derived from Fischer-Tropsch (FT) processes) so as to produce high value diester-based lubricants. In some embodiments, such diester-based lubricants are derived from FT olefins and fatty (carboxylic) acids. In these or other embodiments, the fatty acids can be from a bio-based source (i.e., biomass, renewable source) and/or can be derived from FT alcohols via oxidation.

[0024] Use of enzymes to catalyze and/or mediate formation (derivation) of an epoxide intermediate can provide a number of advantages, such as, but not restricted to, greater specificity, higher process yields, shorter reaction times, and/or more benign reaction conditions. Additionally, such enzymes can be biologically-produced and are generally seen as being environmentally-friendly.

[0025] Because biolubricants and biofuels are increasingly capturing the public's attention and becoming topics of focus for many in the oil industry, the use of biomass in the making of such above-mentioned lubricants could be attractive from several different perspectives. To the extent that biomass is so utilized in the making of the diester-based lubricants of the present invention, such lubricants are deemed to be biolubricants.

2. Definitions

[0026] "Lubricants," as defined herein, are substances (usually a fluid under operating conditions) introduced between two moving surfaces so to reduce the friction and wear

WO 2010/056832

PCT/US2009/064170

between them. Base oils used as motor oils are generally classified by the American Petroleum Institute as being mineral oils (Group I, II, and III) or synthetic oils (Group IV and V). See American Petroleum Institute (API) Publication Number 1509.

[0027] “Pour point,” as defined herein, represents the lowest temperature at which a fluid will pour or flow. See, e.g., ASTM International Standard Test Methods D 5950-96, D 6892-03, and D 97.

[0028] “Cloud point,” as defined herein, represents the temperature at which a fluid begins to phase separate due to crystal formation. See, e.g., ASTM Standard Test Methods D 5773-95, D 2500, D 5551, and D 5771.

[0029] “Centistoke,” abbreviated “cSt,” is a unit for kinematic viscosity of a fluid (e.g., a lubricant), wherein 1 centistoke equals 1 millimeter squared per second ($1 \text{ cSt} = 1 \text{ mm}^2/\text{s}$). See, e.g., ASTM Standard Guide and Test Methods D.2270-04, D 445-06, D 6074, and D 2983.

[0030] With respect to describing molecules and/or molecular fragments herein, “R_n,” where “n” is an index, refers to a hydrocarbon group, wherein the molecules and/or molecular fragments can be linear and/or branched.

[0031] As defined herein, “C_n,” where “n” is an integer, describes a hydrocarbon molecule or fragment (e.g., an alkyl group) wherein “n” denotes the number of carbon atoms in the fragment or molecule.

[0032] The prefix “bio,” as used herein, refers to an association with a renewable resource of biological origin, such resources generally being exclusive of fossil fuels.

[0033] The term “internal olefin,” as used herein, refers to an olefin (i.e., an alkene) having a non-terminal carbon-carbon double bond (C=C). This is in contrast to “α-olefins” which do bear a terminal carbon-carbon double bond.

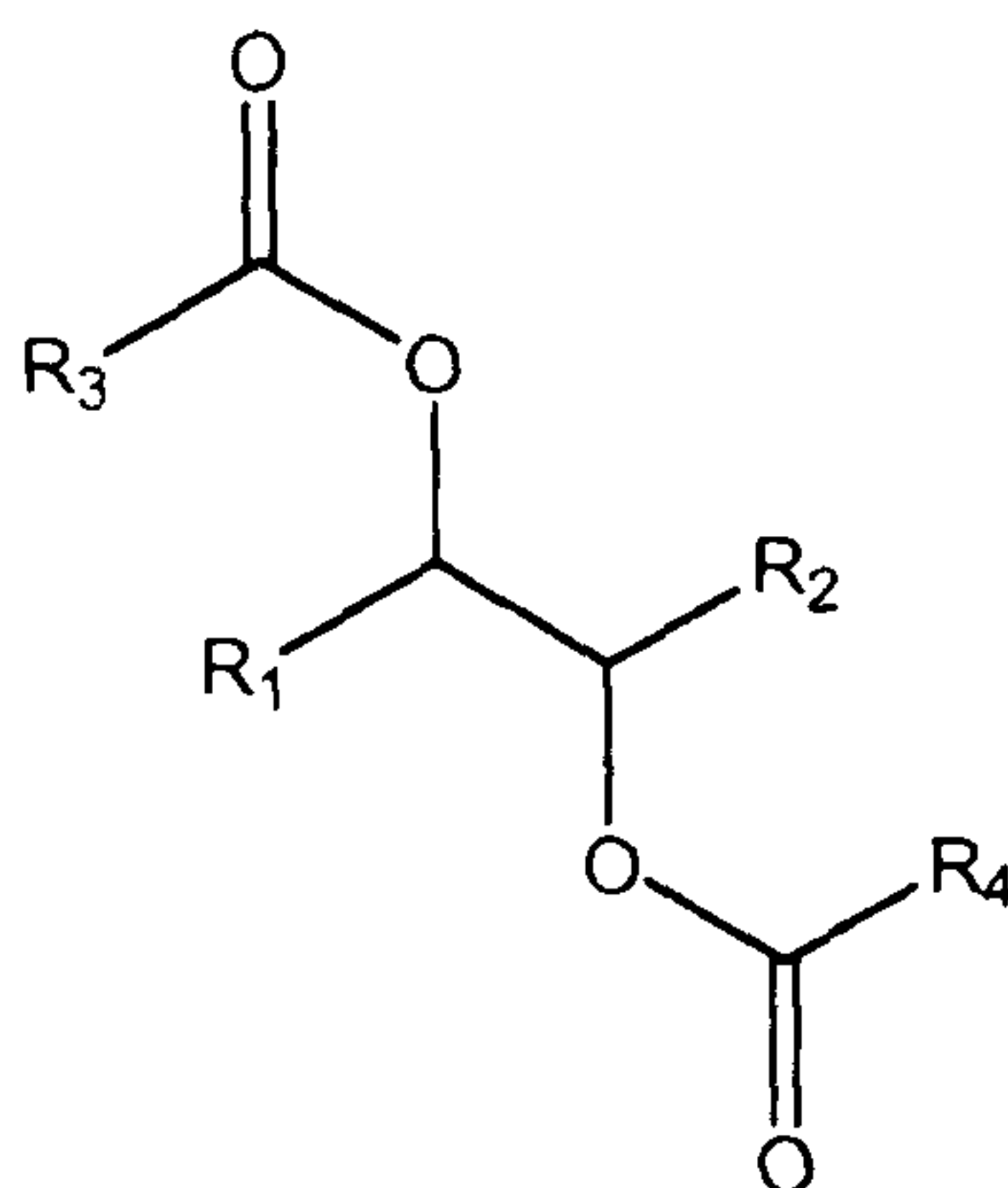
[0034] The term “enzyme,” as used herein, refers to biologically-produced catalyst that enhances the rate at which a particular reaction occurs—often with considerable specificity. Generally such species are proteins. Wherein such enzymes directly catalyze a particular reaction, that reaction is said to be “enzymatically-catalyzed.” Wherein enzymes catalyze the formation and/or consumption of reactants and/or products for a particular reaction, that reaction is said to be “enzymatically-mediated.” Reactions that are enzyme-catalyzed and/or enzyme-mediated are generally termed, “enzymatically-driven” or “enzymatically-directed.”

WO 2010/056832

PCT/US2009/064170

3. Diester Lubricant Compositions

[0035] Methods of the present invention generally provide for diester-based lubricant compositions comprising a quantity of (vicinal) diester species having the following chemical structure:



where R_1 , R_2 , R_3 , and R_4 are the same or independently selected from a C_2 to C_{17} carbon fragment.

[0036] Regarding the above-mentioned diester species, selection of R_1 , R_2 , R_3 , and R_4 can follow any or all of several criteria. For example, in some embodiments, R_1 , R_2 , R_3 , and R_4 are selected such that the kinematic viscosity of the composition at a temperature of 100°C is typically 3 centistokes (cSt) or greater. In some or other embodiments, R_1 , R_2 , R_3 , and R_4 are selected such that the pour point of the resulting lubricant is -20°C or lower. In some embodiments, R_1 and R_2 are selected to have a combined carbon number (i.e., total number of carbon atoms) of from 8 to 18. In these or other embodiments, R_3 and R_4 are selected to have a combined carbon number of from 10 to 34. Depending on the embodiment, such resulting diester species can have a molecular mass between 340 atomic mass units (a.m.u.) and 780 a.m.u.

[0037] In some embodiments, such above-described compositions are substantially homogeneous in terms of their diester component. In some or other embodiments, the diester component of such compositions comprises a variety (i.e., a mixture) of diester species. In some embodiments, the diester-based lubricant composition that is produced comprises at least one diester species derived from a C_8 to C_{18} olefin and a C_6 to C_{14} carboxylic acid.

[0038] In some of the above-described embodiments, the diester-based lubricant composition comprises diester species selected from the group consisting of decanoic acid 2-

WO 2010/056832

PCT/US2009/064170

decanoyloxy-1-hexyl-octyl ester and its isomers, tetradecanoic acid-1-hexyl-2-tetradecanoyloxy-octyl esters and its isomers, dodecanoic acid 2-dodecanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-hexy-octyl ester and its isomers, octanoic acid 2-octanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-pentyl-heptyl ester and isomers, octanoic acid 2-octanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid 2-decanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid-2-decanoyloxy-1-pentyl-heptyl ester and its isomers, dodecanoic acid-2-dodecanoyloxy-1-pentyl-heptyl ester and isomers, tetradecanoic acid 1-penty-2-tetradecanoyloxy-heptyl ester and isomers, tetradecanoic acid 1-butyl-2-tetradecanoyloxy-hexyl ester and isomers, dodecanoic acid-1-butyl-2-dodecanoyloxy-hexyl ester and isomers, decanoic acid 1-butyl-2-decanoyloxy-hexyl ester and isomers, octanoic acid 1-butyl-2-octanoyloxy-hexyl ester and isomers, hexanoic acid 1-butyl-2-hexanoyloxy-hexyl ester and isomers, tetradecanoic acid 1-propyl-2-tetradecanoyloxy-pentyl ester and isomers, dodecanoic acid 2-dodecanoyloxy-1-propyl-pentyl ester and isomers, decanoic acid 2-decanoyloxy-1-propyl-pentyl ester and isomers, octanoic acid 1- 2-octanoyloxy-1-propyl-pentyl ester and isomers, hexanoic acid 2-hexanoyloxy-1-propyl-pentyl ester and isomers, and mixtures thereof.

[0039] It is worth noting that, in most applications, the above-described esters and their compositions are unlikely to be used as lubricants by themselves, but are usually used as blending stocks. As such, esters with higher pour points may also be used as blending stocks with other lubricant oils since they are very soluble in hydrocarbons and hydrocarbon-based oils.

[0040] Regarding the properties of the above-mentioned diester-based lubricants, such compositions typically have a viscosity of 3.8-6.0 cSt at 100°C and a viscosity index (VI) of 120-170. Preferably, the pour point of such compositions is less than -12°C, and more preferably less than -18°C. Additionally, such compositions preferably have an oxidator BN value (oxidator BN test, *vide infra*) of greater than 12 hours, and more preferably greater than 20 hours.

[0041] Note that the oxidator BN test referred to above is a test measuring resistance to oxidation by means of a Dornite-type oxygen absorption apparatus, wherein the conditions are generally one atmosphere of pure oxygen at 340°F, and wherein one reports the hours to absorption of 1000 ml of O₂ by 100 grams of oil. For more information on this test, see, e.g., Stangeland et al., United States Patent No. 3,852,207.

WO 2010/056832

PCT/US2009/064170

4. Methods of Making Diester Lubricants

[0042] As mentioned above, the present invention is generally directed to methods of making the above-described lubricant compositions, wherein such methods make use of enzymes to catalyze and/or mediate the formation of intermediate species (epoxides) that are key to generating the ester-based lubricant compositions of the present invention.

Methods of a First Type

[0043] Referring to the flow diagram shown in **Fig. 1**, in some embodiments processes for making the above-mentioned (vicinal) diester species, typically having lubricating base oil viscosity and pour point (either by themselves or in concert with a lubricant formulation of which they are part), comprise the following steps: (Step 101) epoxidizing an olefin (or quantity of olefins) having a carbon number of from 8 to 18 to form an epoxide comprising an epoxide ring, wherein such epoxidizing is enzymatically-driven; and (Step 102) directly esterifying (subjecting to esterification, i.e., diacylating) the epoxide with an C₂ to C₁₈ carboxylic acid to form a diester species. Generally, lubricant compositions comprising such diester species have a viscosity of 3 centistokes or more at a temperature of 100°C. It will be appreciated by those of skill in the art that, in the steps of epoxidizing and esterifying, a plurality of olefins and epoxides, respectively, are typically so reacted, so as to effect the production of a plurality of diester species.

[0044] In some embodiments, where a quantity of such diester species is formed, the quantity of diester species can be substantially homogeneous, or it can comprise a mixture of two or more different such diester species.

[0045] In some embodiments, the diester so formed is mixed or admixed with a base oil selected from the group consisting of Group I oils, Group II oils, Group III oils, and mixtures thereof.

[0046] In some such above-described method embodiments, the olefin used is a reaction product of a Fischer-Tropsch process. In some or other embodiments, the olefin used is derived from the pyrolysis of waste plastic. Generally speaking, however, the source of the olefin(s) is not particularly limited.

[0047] In some embodiments, the olefin is an α -olefin (i.e., an olefin having a double bond at a chain terminus). In such embodiments, it is often necessary to isomerize the olefin so as to internalize the double bond. Such isomerization is typically carried out catalytically using

WO 2010/056832

PCT/US2009/064170

a catalyst such as, but not limited to, crystalline aluminosilicate and like materials and aluminophosphates. See, e.g., United States Patent Nos. 2,537,283; 3,211,801; 3,270,085; 3,327,014; 3,304,343; 3,448,164; 4,593,146; 3,723,564 and 6,281,404; the last of which claims a crystalline aluminophosphate-based catalyst with 1-dimensional pores of size between 3.8 Å and 5 Å.

[0048] As an example of such above-described isomerizing and as indicated in Scheme 1 (Fig. 2), Fischer-Tropsch alpha olefins (α -olefins) can be isomerized to the corresponding internal olefins followed by epoxidation (*vide infra*). The epoxides can then be transformed to the corresponding diesters via direct (di)-esterification with the appropriate carboxylic acids. It is typically necessary to convert alpha olefins to internal olefins because diesters of alpha olefins, especially short chain alpha olefins, tend to be solids or waxes. "Internalizing" alpha olefins followed by transformation to the diester functionalities introduces branching along the chain which reduces the pour point of the intended products. The ester groups with their polar character would further enhance the viscosity of the final product. Introduction of the ester groups as branches will also increase the carbon number and hence viscosity. It can also decrease the associated pour and cloud points. It is typically preferable to have a few longer branches than many short branches, since increased branching tends to lower the viscosity index (VI).

[0049] Regarding the step of epoxidizing (i.e., the epoxidation step), in some embodiments, the above-described olefin (preferably an internal olefin) can be reacted with a peroxide (e.g., H₂O₂) or a peroxy acid (e.g., peroxyacetic acid) so as to generate an epoxide. See, e.g., D. Swern, in *Organic Peroxides Vol. II*, Wiley-Interscience, New York, 1971, pp. 355-533; and B. Plesnicar, in *Oxidation in Organic Chemistry, Part C*, W. Trahanovsky (ed.), Academic Press, New York 1978, pp. 221-253. Enzymes can also be used to catalyze and/or mediate this epoxidation, wherein suitable enzymes include, but are not limited to, lipolytic enzymes such as lipases, as described in M. Klaas et al., "Chemoenzymatic Epoxidation of Unsaturated Fatty Acid Esters and Plant Oils," J. Am. Oil Chem. Soc., vol. 73(11), pp. 1453-1457, 1996; and M. Klaas et al., "Complete and partial epoxidation of plant oils by lipase-catalyzed perhydrolysis," vol. 9(2), pp. 125-132, 1999. Chemoenzymatic epoxidation of olefins has also been accomplished using cytochrome P450, as described by Farinas et al., "Alkene epoxidation catalyzed by cytochrome P450 BM-3 139-3," Tetrahedron, vol. 60, pp. 525-528, 2004. Such enzymatic epoxidation of olefins is typically done in the presence of

WO 2010/056832

PCT/US2009/064170

carboxylic (fatty) acids, wherein the carboxylic acids are typically present in catalytic amounts. While not intending to be bound by theory, it is believed that the carboxylic acids are converted to their corresponding peroxy acids, which in turn effects the epoxidation of the olefin. See, e.g., Bjorkling et al., "Lipase-mediated formation of peroxycarboxylic acids used in catalytic epoxidation of alkenes," J. Chem. Soc., Chem. Commun., pp. 1301-1303, 1990; and V. Skouridon et al., "Lipase-mediated epoxidation of α -pinene," J. Molecular Catalysis B, vol. 21, pp. 67-69, 2003. Generally, such enzyme catalysts reduce the amount of peroxide/ peroxy acid required to effect epoxidations. An exemplary lipase is an immobilized lipase product based on a lipase from *Candida Antarctica*. This exemplary immobilized lipase is sold under the trade name NOVOZYME 435.

[0050] Regarding the step of directly esterifying (i.e., the esterification step), in some embodiments this step is carried out in the presence of a catalyst. Such catalyst species can include, but are not limited to, H_3PO_4 , H_2SO_4 , sulfonic acid, Lewis acids, silica and alumina-based solid acids, Amberlyst, tungsten oxide, and mixtures and combinations thereof, and the like.

[0051] In some such above-described method embodiments, the carboxylic acid can be derived from alcohols generated by a Fischer-Tropsch process and/or it can be a bio-derived fatty acid. Note that the carboxylic acids can be of a single type (e.g., length), or they can be a mixture of types. Additionally, in some embodiments, quantities of carboxylic acid anhydride can also be utilized together with the carboxylic acid in the esterification.

[0052] In some embodiments, during the step of directly esterifying, efforts are made to remove water produced as a result of the esterifying process. Such efforts can positively impact the diester yield.

[0053] Regardless of the source of the olefin, in some embodiments, the carboxylic acid used in the above-described method is derived from biomass. In some such embodiments, this involves the extraction of some oil (e.g., triglyceride) component from the biomass and hydrolysis of the triglycerides of which the oil component is comprised so as to form free carboxylic acids.

Methods of a Second Type

[0054] Referring to the flow diagram shown in **Fig. 3**, in some embodiments processes (methods) for making the above-mentioned (vicinal) diester species, typically having

WO 2010/056832

PCT/US2009/064170

lubricating base oil viscosity and pour point, comprise the following steps: (Step 301) epoxidation of an olefin to form an epoxide having a carbon number of from 8 to 18, wherein such epoxidation is catalyzed and/or mediated by one or more enzymes; (Step 302) conversion of the epoxide to form a diol; and (Step 303) esterification of the diol with a C₂ to C₁₈ carboxylic acid to form a diester suitable for use as, and/or for inclusion in, lubricant compositions that have viscosity and pour point operable for use as a lubricant. Additionally, such epoxidizing and direct esterifying are typically carried out on a plurality of olefins and epoxides, respectively.

[0055] Embodiments of the present invention utilizing methods of the second type are generally analogous to those of the first type (*vide supra*) for Step 301, but diverge somewhat at Steps 302 and 303; such steps being where the epoxide is converted to a diol, and where the diol is converted to a diester. Accordingly, only the differences are highlighted below.

[0056] Regarding the step of epoxide ring opening to the corresponding diol, this step can be acid-catalyzed or base-catalyzed hydrolysis. Exemplary acid catalysts include, but are not limited to, mineral-based Brønsted acids (e.g., HCl, H₂SO₄, H₃PO₄, perhalogenates such as HClO₄, etc.), Lewis acids (e.g., TiCl₄ and AlCl₃) solid acids such as acidic aluminas and silicas or their mixtures, and the like. See, e.g., Chem. Rev. vol. 59, p. 737, 1959; and Angew. Chem. Int. Ed., vol. 31, p. 1179, 1992. Based-catalyzed hydrolysis typically involves the use of bases such as aqueous solutions of sodium or potassium hydroxide.

[0057] Regarding the step of esterifying (esterification), an acid is typically used to catalyze the reaction between the -OH groups of the diol and the carboxylic acid(s). Suitable acids include, but are not limited to, sulfuric acid (Munch-Peterson, Org. Synth., V, p. 762, 1973), sulfonic acid (Allen and Sprangler, Org Synth., III, p. 203, 1955), hydrochloric acid (Eliel et al., Org Synth., IV, p. 169, 1963), and phosphoric acid (among others). In some embodiments, the carboxylic acid used in this step is first converted to an acyl chloride (via, e.g., thionyl chloride or PCl₃). Alternatively, an acyl chloride could be employed directly. Wherein an acyl chloride is used, an acid catalyst is not needed and a base such as pyridine, 4-dimethylaminopyridine (DMAP) or triethylamine (TEA) is typically added to scavenge any HCl produced. When pyridine or DMAP is used, it is believed that these amines also act as a catalyst by reacting with acyl chloride, thereby forming acyl-pyridinium and acyl-4-dimethylaminopyridinium derivatives, species which are generally more reactive acylating

WO 2010/056832

PCT/US2009/064170

intermediates. See, e.g., Fersh et al., J. Am. Chem. Soc., vol. 92, pp. 5432-5442, 1970; and Hofle et al., Angew. Chem. Int. Ed. Engl., vol. 17, p. 569, 1978.

[0058] As an example of such above-described isomerizing and as indicated in Scheme 2 (Fig. 4), Fischer-Tropsch alpha olefins (α -olefins) can be isomerized to the corresponding internal olefins followed by epoxidation (*vide infra*). The epoxides can then be transformed to the corresponding diesters via conversion to diols that are then esterified with the appropriate carboxylic acids. It is typically necessary to convert alpha olefins to internal olefins because diesters of alpha olefins, especially short chain alpha olefins, tend to be solids or waxes. "Internalizing" alpha olefins followed by transformation to the diester functionalities introduces branching along the chain which reduces the pour point of the intended products. The ester groups with their polar character would further enhance the viscosity of the final product. Adding ester branches will increase the carbon number and hence viscosity. It can also decrease the associated pour and cloud points. It is typically preferable to have a few longer branches than many short branches, since increased branching tends to lower the viscosity index.

5. Variations

[0059] Variations (i.e., alternate embodiments) on the above-described lubricant compositions include, but are not limited to, utilizing mixtures of isomeric olefins and or mixtures of olefins having a different number of carbons. This leads to diester mixtures in the product compositions. Variations on the above-described processes further include, but are not limited to, using carboxylic acids derived from FT alcohols by oxidation.

[0060] The advantages of the methods of the present invention notwithstanding, in some embodiments, it may be advantageous to combine the methods of the first and second types to provide methods that employ both a direct esterification of the epoxide and esterification that first converts the epoxide to a diol.

WO 2010/056832

PCT/US2009/064170

6. Examples

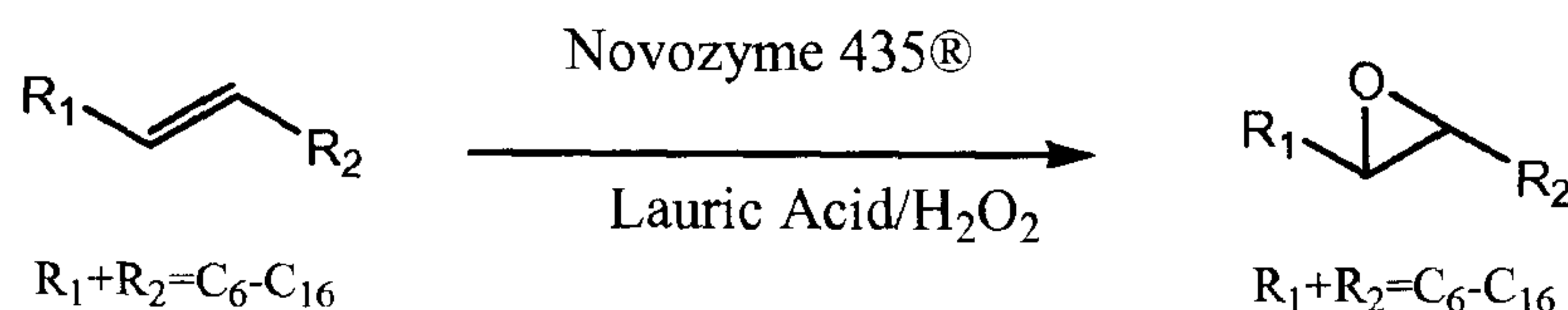
[0061] The following examples are provided to demonstrate, and/or more fully illustrate, particular embodiments of the present invention. It should be appreciated by those of skill in the art that the methods disclosed in the examples which follow merely represent exemplary embodiments of the present invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present invention.

EXAMPLE 1

[0062] This Example serves to illustrate the epoxidation of tetradecenes to form tetradecene epoxides via an enzymatically-driven route, and the subsequent esterification of the tetradecene epoxides to form diester species operable for use in/as diester-based lubricant compositions, in accordance with some embodiments of the present invention.

Formation of Epoxide Intermediates

[0063] Enzymatic epoxidation of olefins was done according to the general procedure described below for the epoxidation of tetradecenes. Below, is a reaction that is illustrative of the general enzymatic procedure.



[0064] A mixture of 1 mol equivalent of the appropriate olefin, 10 mol % of a carboxylic acid, 1.1 mol equivalent of hydrogen peroxide, and the suitable enzyme (~ 1 mg enzyme/1 mmol olefin) were mixed in toluene (0.5 ml toluene/ 1 mmol olefin). The mixture was shaken at 1100 rpm at a temperature appropriate for the survival of both the enzyme and the hydrogen peroxide. The reaction progress was monitored by measuring the olefins

WO 2010/056832

PCT/US2009/064170

conversion to epoxides by nuclear magnetic resonance (NMR) spectroscopic analysis. In a typical run, using tetradecene as the olefin and Novozyme 435[®] as the enzyme (**Fig. 5**, Scheme 3), a mixture of tetradecenes (1 mole equivalent), 10 mol% lauric acid, 1.1 mole equivalent of hydrogen peroxide (50 wt% H₂O₂ in water), and 2-10 grams of Novozyme 435[®] (liquid form or immobilized on poly-acrylate resin)/1 mol equivalent tetradecene olefin were mixed in toluene (2M concentration with respect to olefins). The mixture was shaken at ~1100 rpm at ~50-55°C and the reaction was monitored with NMR spectroscopic analysis. The product was separated from the enzyme by filtration and toluene was removed on a rotary evaporator. At a 1.5 liter scale, the reaction resulted in > 99% olefin conversion to the desired epoxide mixture with < 0.5% unreacted olefins and little lauric acid.

Direct Esterification of Epoxides to the Corresponding Diesters

[0065] In a reaction flask, 393 grams (1.85 mol) of a mixture of tetradecene epoxides, derived by the enzymatic route described above and 1148 grams (5.73 mol) lauric acid was added at room temperature. The resulting mixture was heated to 160°C with N₂ bubbling through for one hour, then H₃PO₄ (17.2 grams, 85%, 0.15 mol) was added and the mixture was heated for an additional 5 hours. After such time the reaction was complete and was allowed to cool gradually to room temperature. The mixture was washed with water 1000 ml, separated, and then dried with MgSO₄. The mixture was filtered and distilled at 160-180°C under vacuum of 2 mm Hg to remove excess lauric acid. Distillation and further water washing and mild caustic treatment to remove any residual lauric acid yielded 1000 gm of the desired product. The reaction is depicted in Scheme 4 (**Fig. 6**). The diester was hydrogenated to remove any residual double bonds that may exist in trace amounts due to unreacted starting olefins or which may have formed by elimination of some of the hydroxyl groups under the acidic reaction conditions.

[0066] Table 1 (**Fig. 7**) compares lubrication properties of diesters derived from tetradecene epoxides (derived enzymatically) with diesters derived from the diols (derived by conventional methods) of the same olefinic mixture.

EXAMPLE 2 (COMPARATIVE)

[0067] This Example serves to illustrate the epoxidation of tetradecenes to form tetradecene epoxides, and the subsequent esterification of the tetradecene epoxides to form diester species

WO 2010/056832

PCT/US2009/064170

operable for use in/as diester-based lubricant compositions, wherein said epoxidation is not catalyzed and/or mediated by an enzyme species.

[0068] Tetradecenes were epoxidized as follows using a general procedure for the epoxidation of 7,8-tetradecene. To a stirred solution of 143 grams (0.64 mole) of 77% mCPBA (meta-chloroperoxybenzoic acid) in 500 mL chloroform, 100 grams (0.51 mol) of 7,8-tetradecene in 200 mL chloroform was added drop-wise over a 45-minute period. The resulting reaction mixture was stirred overnight. The resulting milky solution was subsequently filtered to remove meta-chloro-benzoic acid that formed therein. The filtrate was then washed with a 10% aqueous solution of sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. The reaction afforded the desired epoxide (isomers of n-tetradecene epoxides) as colorless oil in 93% yield.

[0069] The isomers of n-tetradecene epoxides (10.6 grams, 50 mmol) were mixed with lauric acid (30 grams, 150 mmol) and 85% H_3PO_4 (0.1 grams, 0.87 mmol). The mixture was stirred and bubbled/purged with nitrogen at 150°C for 20 hours. Excess lauric acid was removed from the product first by recrystallization in hexane with subsequent filtration at -15°C, and then by adding a calculated amount of 1N NaOH solution and filtering out the sodium laurate salt. The diester product collected (21.8 grams, 73% yield) was a light yellow, transparent oil. The oil comprised a mixture of the diester species 1-7 depicted in Fig. 8.

EXAMPLE 3

[0070] This Example serves to illustrate the direct esterification of 1-dodecene epoxide (2-decyl-oxirane) to yield a diester species, in accordance with some embodiments of the present invention.

[0071] Quantities of 1-dodecene epoxide (9.2 grams, 50 mmol) and octanoic acid (14.4 grams, 100 mmol) were dissolved in 12 mL toluene, and 85% H_3PO_4 (0.3 grams, 0.87 mmol) was added. The mixture was stirred and bubbled/purged with nitrogen at 140°C for 23 hours. The mixture was subsequently washed with a K_2CO_3 -saturated solution, filtered and separated to remove the acids, the organic layer was dried by anhydrous MgSO_4 and

WO 2010/056832

PCT/US2009/064170

evaporated under reduced pressure. Referring to **Fig. 9**, the diester product **8**, octanoic acid 2-octanoyloxy-dodecyl ester, (18 grams, 83% yield) was a transparent, colorless oil.

EXAMPLE 4

[0072] This Example serves to illustrate synthesis and isolation of a diol, and subsequent esterification of said diol, en route to synthesis of a diester species, in accordance with some embodiments of the present invention.

Diol Preparation and Isolation

[0073] In a 3-neck 1 mL reaction flask equipped with an overhead stirrer and an ice bath, 75 mL of 30% hydrogen peroxide were added to 300 mL of 96% formic acid. To this mixture, 100 grams (0.51 mole) of 7-tetradecene (purchased from Aldrich Chemical Co.) was added slowly over a 30 minute period via a dropping funnel. Once the addition of the olefin was complete, the reaction was allowed to stir while cooling with the ice-bath to prevent rise in the temperature above 40-50°C for 2 hrs. The ice-bath was then removed and the reaction was stirred at room temperature overnight. The reaction mixture was concentrated with a rotary evaporator in a hot water bath at ~30 torr to remove most of the water and formic acid. Then, 100 mL of ice-cold 1 M solution of sodium hydroxide was added very slowly (in small portions) and carefully to the remaining residue of the reaction. Once all the sodium hydroxide solution was added, the mixture was allowed to stir for an additional 45-60 minutes at room temperature. The mixture was diluted with 500 mL ethyl acetate and transferred to a separatory funnel. The organic layer was sequestered and the aqueous layer was extracted 3 times (3x200 mL) with ethyl acetate. The ethyl acetate extracts were combined and dried over anhydrous MgSO₄. Filtration, followed by concentration on a rotary evaporator at reduced pressure in a hot water bath gave the desired diol as white powder in 88% yield (95 grams). The produced and isolated diol (tetradecane-7,8-diol) was characterized by nuclear magnetic resonance (NMR) spectroscopy and gas-chromatography/mass spectrometry (GC/MS).

Conversion of the Diol to a Diester

[0074] What follows serves to illustrate synthesis of diester **10** (decanoic acid 2-decanoyloxy-1-hexyl-octyl ester) from tetradecane-7,8-diol (see above). **Fig. 10** depicts

WO 2010/056832

PCT/US2009/064170

diester **10**, as well as diester **9** (hexanoic acid 2-hexanoyloxy-1-hexyl-octyl ester), the latter being similarly prepared by using hexanoic acid or an anhydrous variant thereof.

[0075] In a 3-neck 1 L reaction flask equipped with an overhead stirrer, reflux condenser and a dropping funnel, 50 grams (0.23 mol) of tetradecane-7,8-diol (prepared above) and 60 grams (0.59 mol) triethylamine and a catalytic amount of dimethylaminopyridine (6.5 grams; 0.052 mol) were mixed in 500 mL anhydrous hexane. The solution was cooled down with an ice bath. To this solution 97 grams (0.51 mol) decanoyl chloride was added drop-wise over a 15 minute period. Once the addition was complete, the ice bath was removed and the reaction was allowed to stir overnight. Then, an additional 12 grams of the decanoyl chloride was added and the reaction was refluxed overnight. The resulting "milky" reaction solution was neutralized with water. The resulting two layer mixture was then transferred to a separatory funnel. The organic (top) layer was separated and washed with 2x500 mL water. The aqueous layer was extracted with 3x300 mL ether. The ether extracts and the original organic layer were combined, dried over MgSO_4 , filtered, and concentrated over a rotary evaporator at reduced pressure. The resulting residue was analyzed by NMR and infrared (IR) spectroscopies and GC/MS. Such analysis confirmed the presence of decanoic acid. The mixture was treated with 3 M aqueous solution of sodium carbonate (to neutralize the acid impurity) in 500 mL hexane. The hexane layer was dried over MgSO_4 , filtered and concentrated on a rotary evaporator to give the desired diester product as a colorless viscous oil with a sweet odor in 81% yield (100.5 grams). GC/MS indicated the presence of less than 1% residual acid in the product.

7. Summary

[0076] In summary, the present invention provides for methods (processes) of making diester-based lubricant compositions, wherein such methods generally comprise a step of enzymatically-driving the formation of an epoxide intermediate. In some embodiments, the methods for making such diester-based lubricants utilize a biomass precursor and/or low value Fischer-Tropsch (FT) olefins and/or alcohols so as to produce high value diester-based lubricants. In some embodiments, such diester-based lubricants are derived from FT olefins and fatty acids. The fatty acids can be from a bio-based source (i.e., biomass, renewable source) or can be derived from FT alcohols via oxidation.

WO 2010/056832

PCT/US2009/064170

[0077] All patents and publications referenced herein are hereby incorporated by reference to the extent not inconsistent herewith. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.

WO 2010/056832

PCT/US2009/064170

WHAT IS CLAIMED:

1. A process comprising:
 - a) epoxidizing an olefin having a carbon number of from 8 to 18 to form an epoxide comprising an epoxide ring, wherein such epoxidizing is enzymatically-driven; and
 - b) esterifying the epoxide to form a diester species having viscosity and pour point suitable for use as a lubricant or component thereof.
2. The process of Claim 1, wherein the step of esterifying the epoxide proceeds directly with a C₂ to C₁₈ carboxylic acid.
3. The process of Claim 1, wherein the step of esterifying the epoxide proceeds via the following sub-steps:
 - (i) opening the epoxide ring of the epoxide to form a diol; and
 - (ii) esterifying the diol with a C₂ to C₁₈ esterification agent to form a diester species having viscosity and pour point suitable for use as a lubricant or component thereof, and wherein said esterification agent is selected from the group consisting of carboxylic acids, acyl chlorides, and combinations thereof.
4. The process of Claim 2 or 3, wherein the olefin is isomerized from an α -olefin to an internal olefin.
5. The process of Claim 4, wherein the olefin is double bond isomerized with an olefin isomerization catalyst.
6. The process of Claim 2 or 3, wherein the step of epoxidizing is further driven by a carboxylic acid and a hydrogen peroxide initiator.

WO 2010/056832

PCT/US2009/064170

7. The process of Claim 6, wherein a lipolytic enzyme is used to mediate epoxidation of the olefin.
8. The process of Claim 7, wherein the lipolytic enzyme is a lipase.
9. The process of Claim 8, wherein the lipase is an immobilized lipase product based on a lipase from *Candida Antarctica*.
10. The process of Claim 2, wherein the step of directly esterifying is catalyzed by the presence of an acid catalyst selected from the group consisting of H₃PO₄, H₂SO₄, sulfonic acid, Lewis acids, silica and alumina-based solid acids, Amberlyst, tungsten oxide, and combinations thereof.
11. The process of Claim 2, wherein the step of directly esterifying additionally comprises the presence of a carboxylic acid anhydride.
12. The process of Claim 3, wherein the step of esterifying is catalyzed by the presence of an acid catalyst, wherein the acid catalyst is selected from the group consisting of H₃PO₄, H₂SO₄, sulfonic acid, Lewis acids, silica and alumina-based solid acids, Amberlyst, tungsten oxide, and combinations thereof.
13. The process of Claim 3, wherein the step of esterifying additionally comprises the presence of a carboxylic acid anhydride.
14. The process of Claim 1, further comprising a step of blending the diester species with one or more other species selected from the group consisting of other diester species, Group I oils, Group II oils, Group III oils, and mixtures thereof.

WO 2010/056832

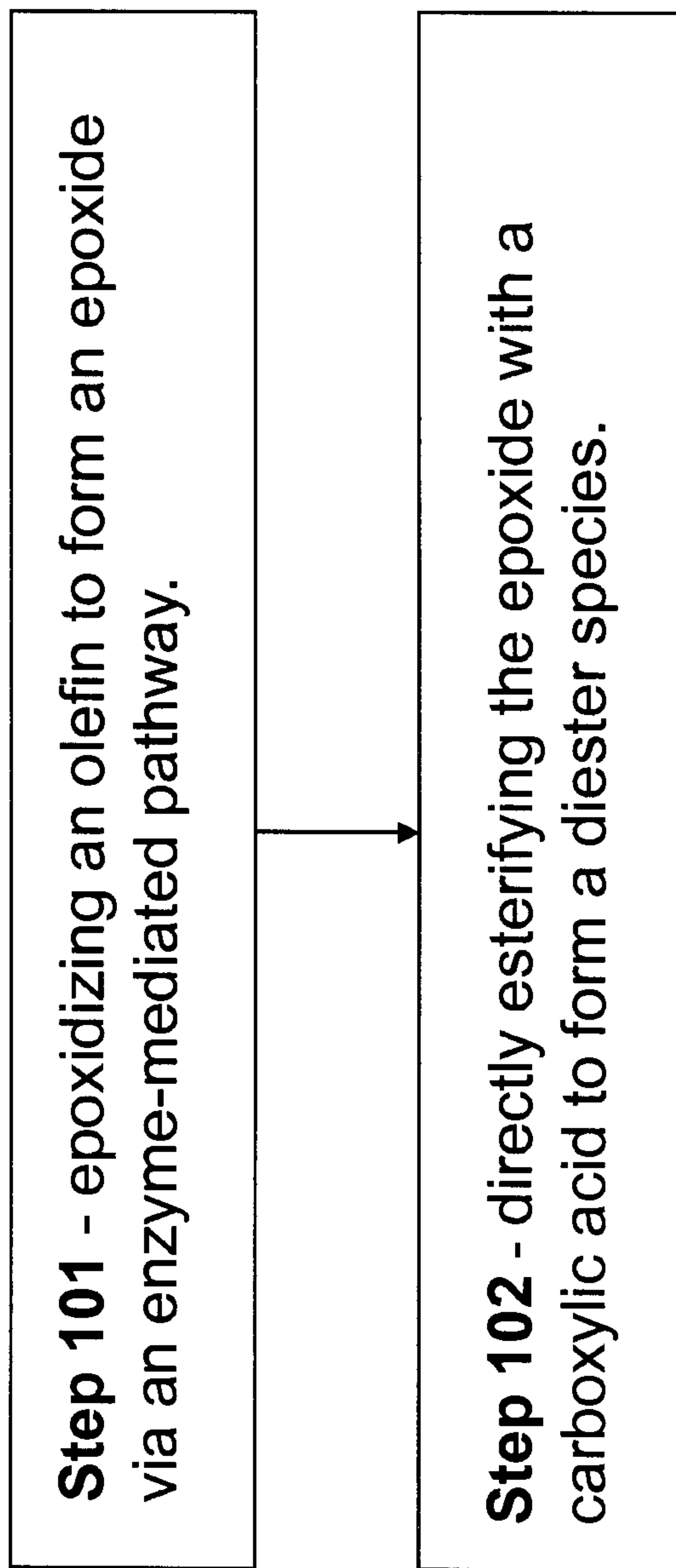
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15. The process of Claim 1, wherein the olefin is a Fischer-Tropsch reaction product.
16. The process of Claim 1, wherein the olefin is derived from the pyrolysis of waste plastic.
17. The process of Claim 1, wherein the diester species formed is selected from the group consisting of decanoic acid 2-decanoyloxy-1-hexyl-octyl ester and its isomers, tetradecanoic acid-1-hexyl-2-tetradecanoyloxy-octyl esters and its isomers, dodecanoic acid 2-dodecanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-hexy-octyl ester and its isomers, octanoic acid 2-octanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-pentyl-heptyl ester and isomers, octanoic acid 2-octanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid 2-decanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid-2-decanoyloxy-1-pentyl-heptyl ester and its isomers, dodecanoic acid-2-dodecanoyloxy-1-pentyl-heptyl ester and isomers, tetradecanoic acid 1-pentyl-2-tetradecanoyloxy-heptyl ester and isomers, tetradecanoic acid 1-butyl-2-tetradecanoyloxy-hexyl ester and isomers, dodecanoic acid-1-butyl-2-dodecanoyloxy-hexyl ester and isomers, decanoic acid 1-butyl-2-decanoyloxy-hexyl ester and isomers, octanoic acid 1-butyl-2-octanoyloxy-hexyl ester and isomers, hexanoic acid 1-butyl-2-hexanoyloxy-hexyl ester and isomers, tetradecanoic acid 1-propyl-2-tetradecanoyloxy-pentyl ester and isomers, dodecanoic acid 2-dodecanoyloxy-1-propyl-pentyl ester and isomers, decanoic acid 2-decanoyloxy-1-propyl-pentyl ester and isomers, octanoic acid 1- 2-octanoyloxy-1-propyl-pentyl ester and isomers, hexanoic acid 2-hexanoyloxy-1-propyl-pentyl ester and isomers, and mixtures thereof.
18. The process of Claim 1, wherein the diester species formed has a viscosity in the range of 3.8 to 6.0 cSt at 100°C and a viscosity index in the range of 120 to 170.
19. The process of Claim 1, wherein the diester species formed has a pour point of less than -12°C.

WO 2010/056832

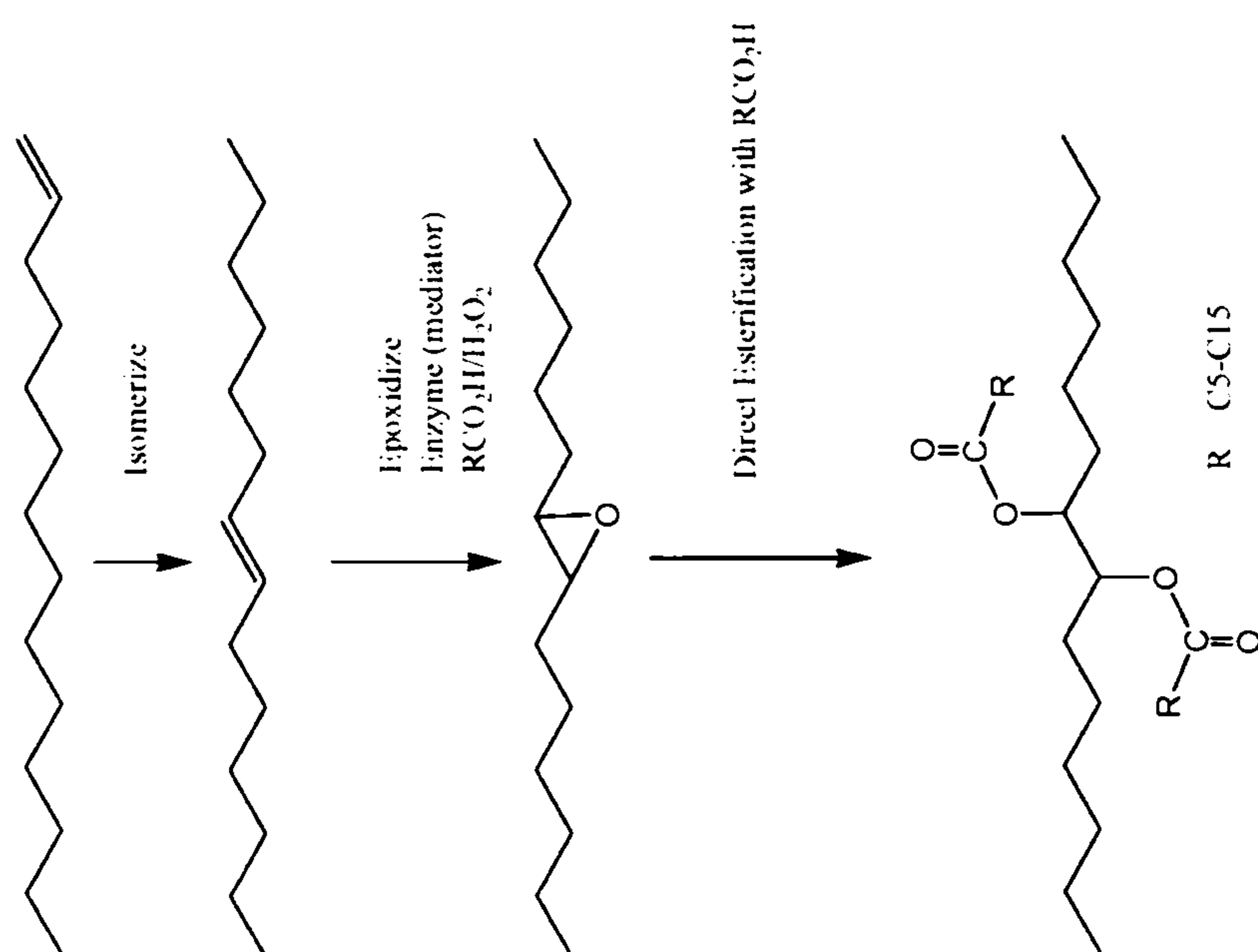
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20. The process of Claim 1, wherein the diester species formed has an oxidator BN value of greater than 12 hours.

**Fig. 1**

WO 2010/056832

PCT/US2009/064170

**Scheme 1****Fig. 2**

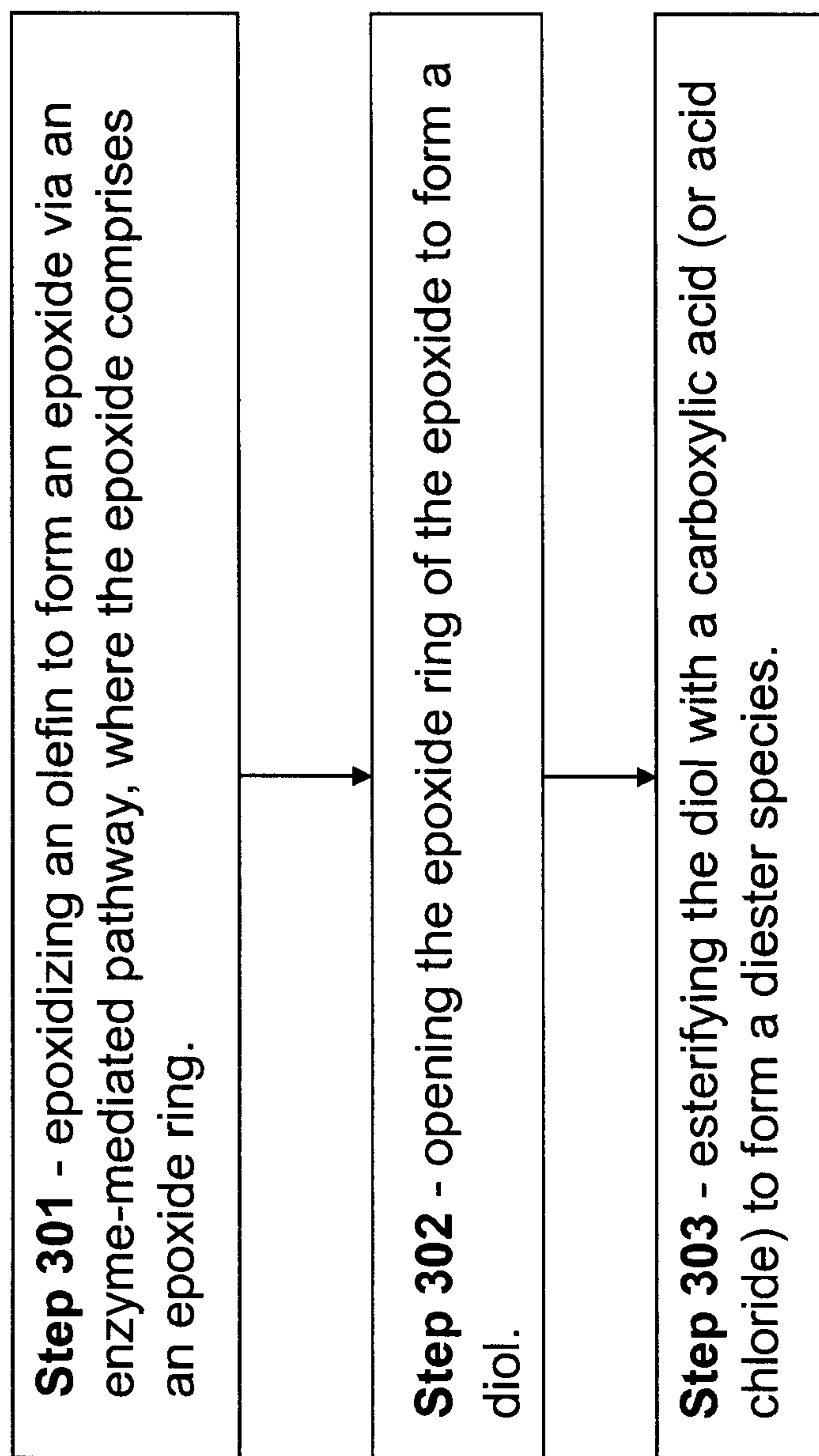
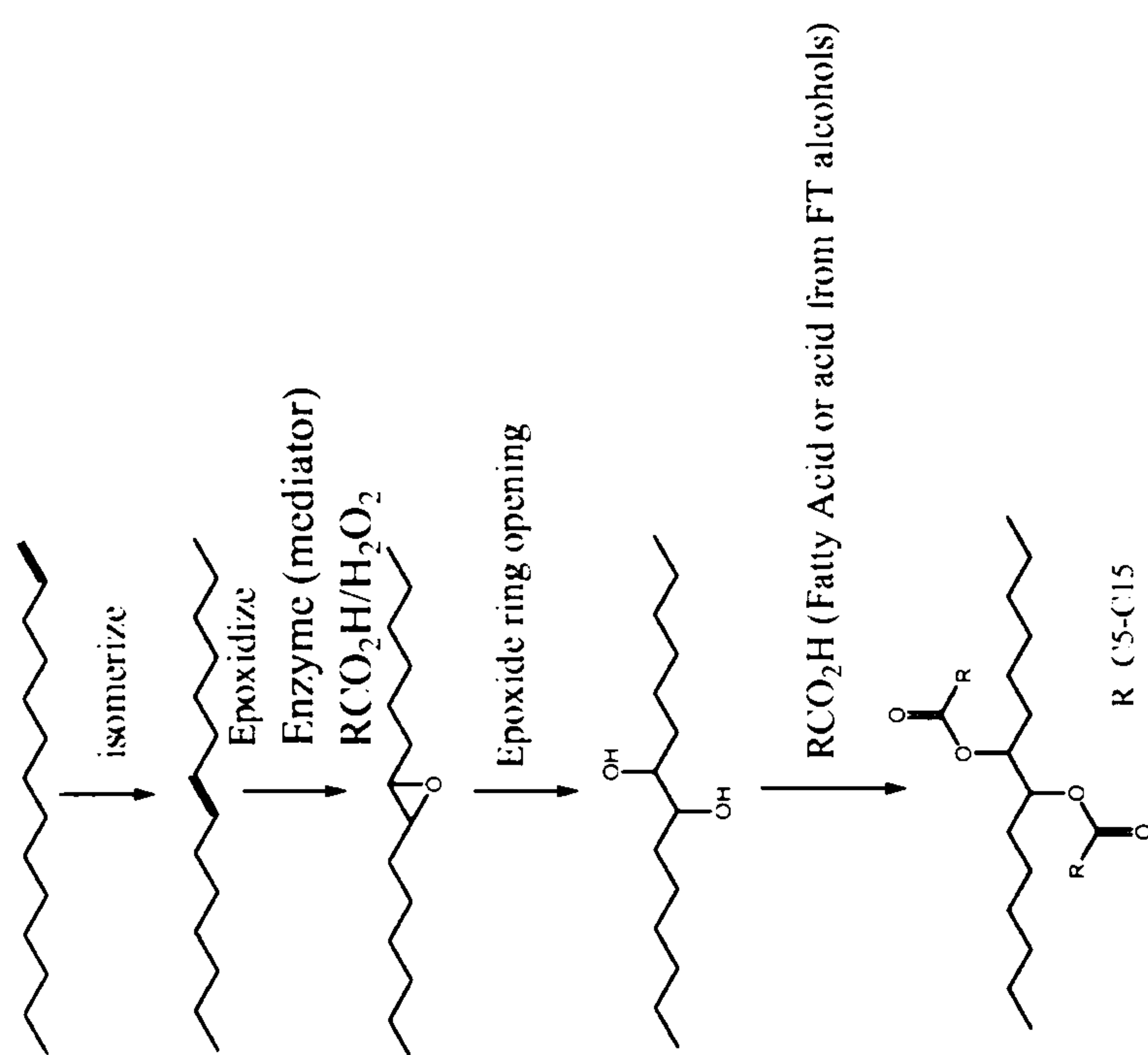
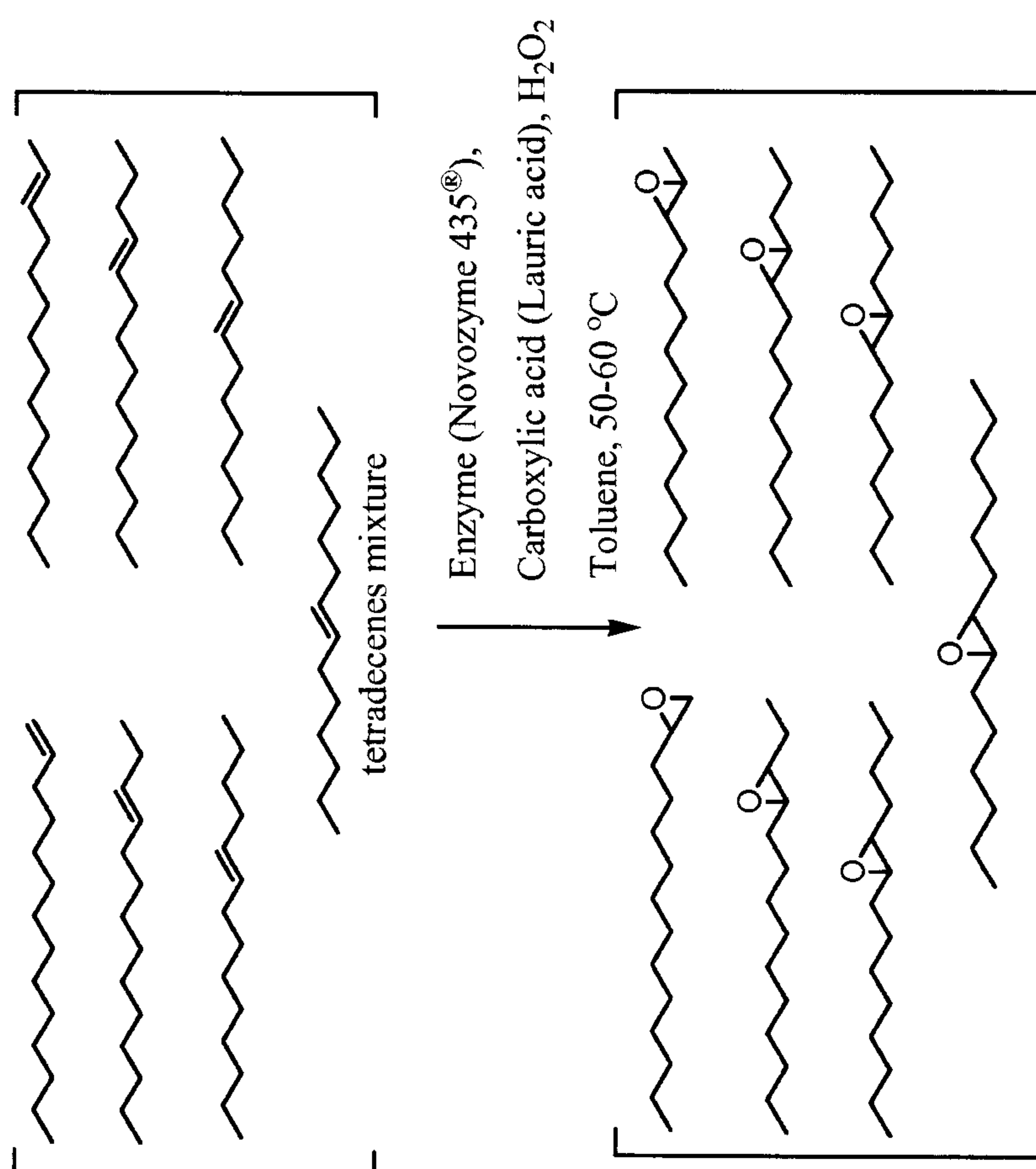


Fig. 3

WO 2010/056832

PCT/US2009/064170

Scheme 2**Fig. 4**

Scheme 3**Fig. 5**

Scheme 4

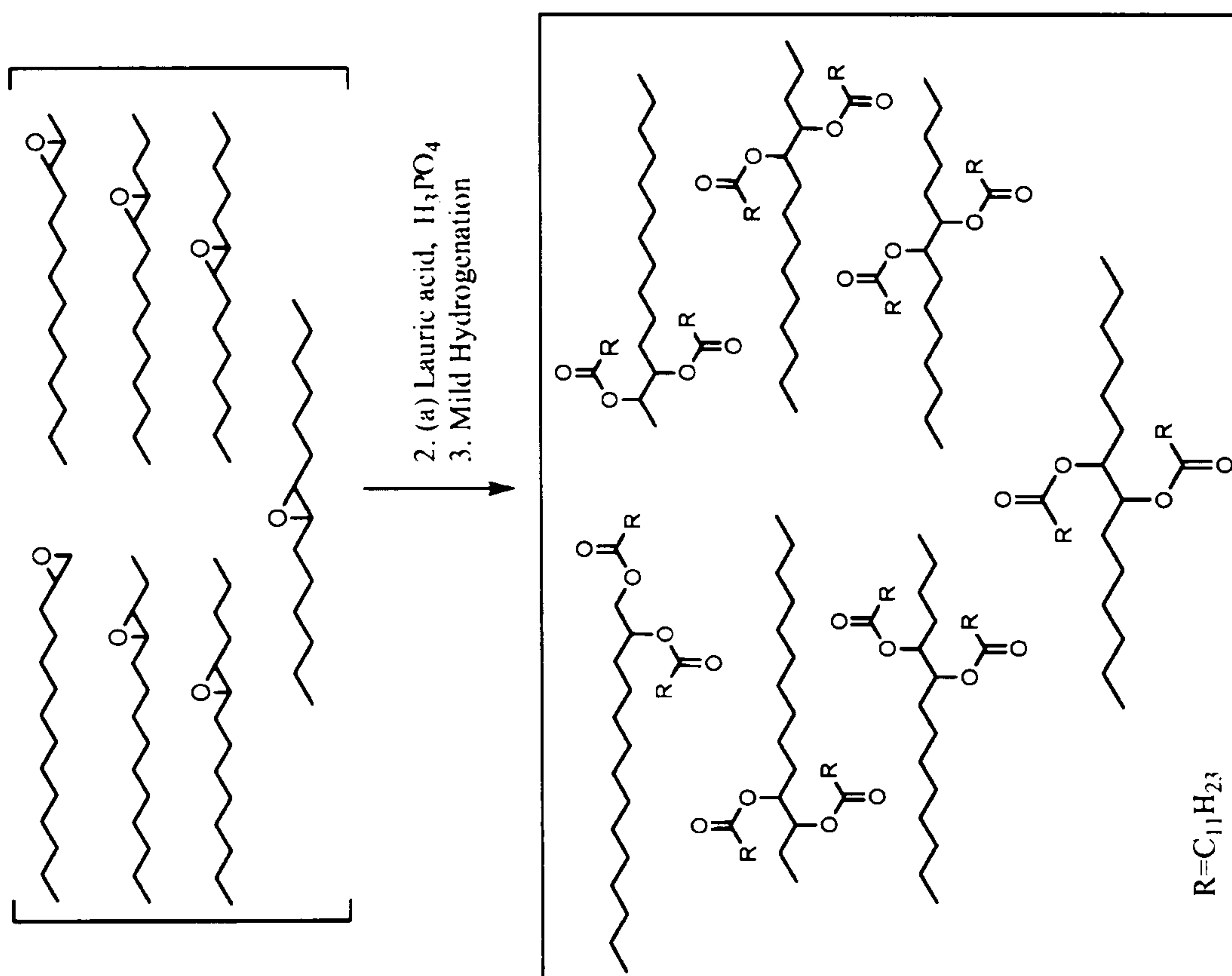


Fig. 6

Table 1

<u>Property</u>	Diesters from tetradecene epoxides	Diesters from tetradecene diols
Pour point (°C)	-27	-28
Cloud point (°C)	-28	-29
Viscosity @ 40°C (cSt)	19.5	19.5
Viscosity @ 100°C (cSt)	4.88	4.4
Viscosity Index	146	140
Oxidator BN, hrs	20.7	20.6

Fig. 7

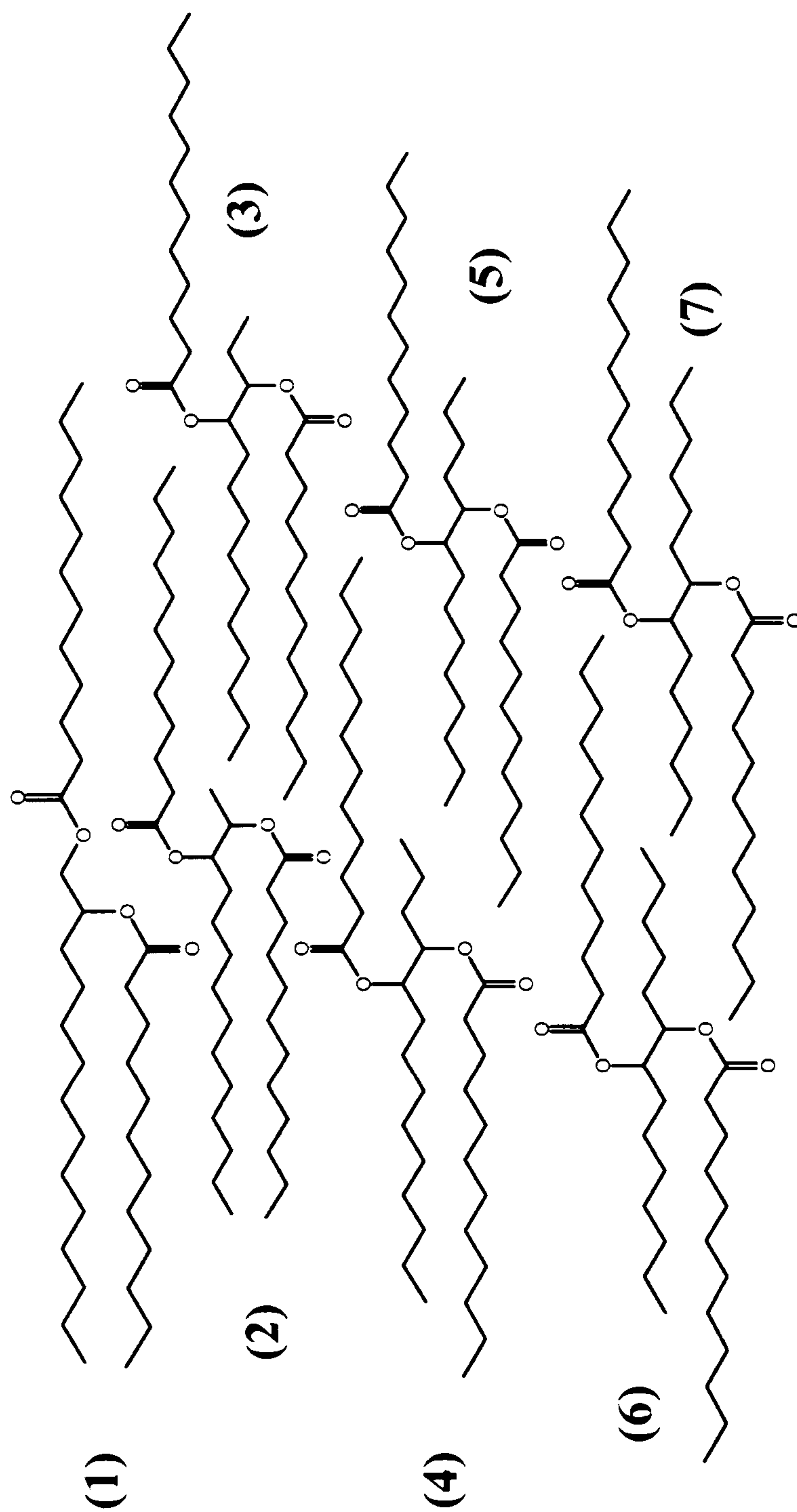


Fig. 8

WO 2010/056832

PCT/US2009/064170

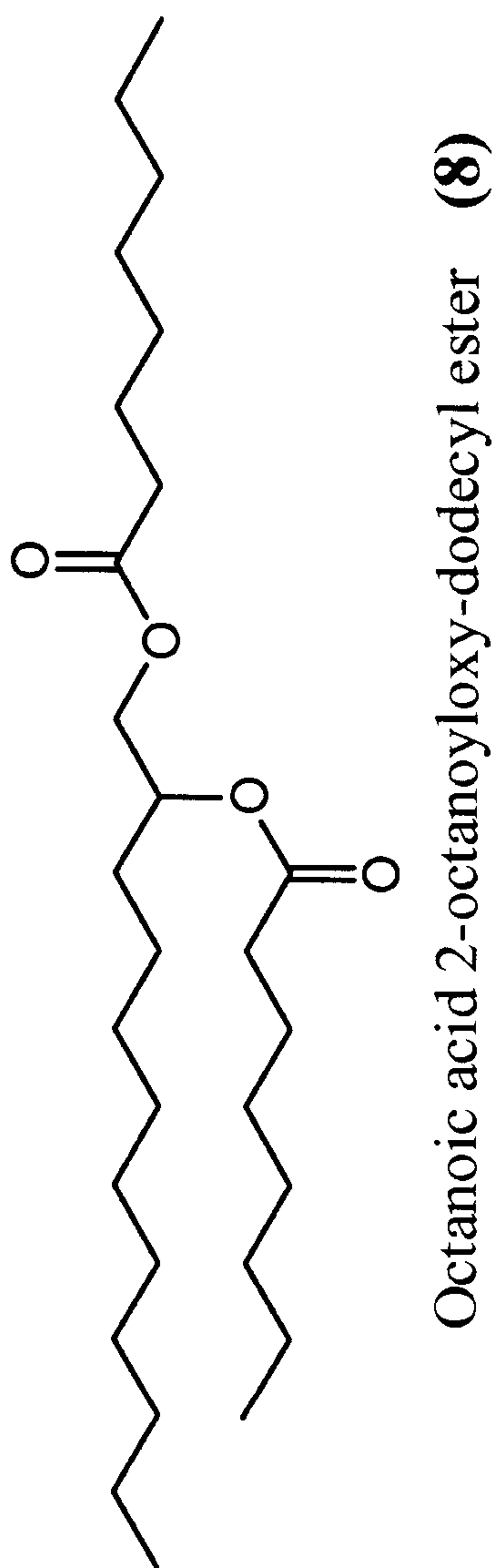
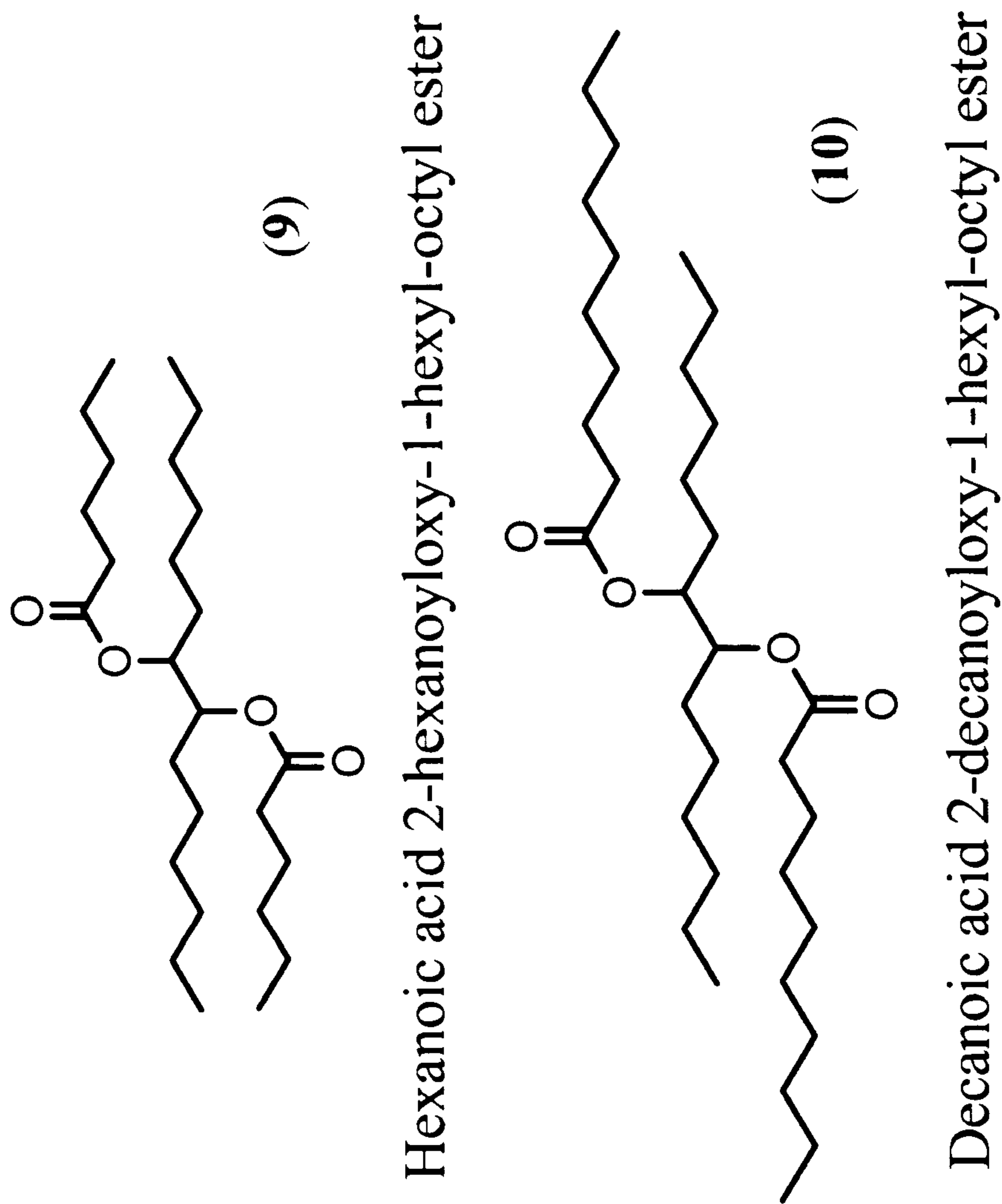


Fig. 9

**Fig. 10**

Step 101 - epoxidizing an olefin to form an epoxide via an enzyme-mediated pathway.



Step 102 - directly esterifying the epoxide with a carboxylic acid to form a diester species.

Fig. 1